

SUMMARY OF THE OFFICE ACTION

- 1) Claim 9 has been rejected under the **first paragraph** provisions of 35 USC 112 as containing matter which was not originally described in the specification.
- 2) Claims 2, 3, 6, 8, 11, 12, 15 and 17 have been finally rejected under 35U.S.C § 102(b) as being anticipated by Berg (5,984,988).
- 3) Claims 4 and 13 have been finally Rejected under 35U.S.C. 103(a) as unpatentable over Berg (5,984,988) in light of Howard (3,916,584) and in further view of the rejections of Claims 2 and 11. The use of dehydrating liquid is commonly practiced and well known in the art.
- 4) Claims 5 and 14 have been finally rejected under 35U.S.C. 103(a) as unpatentable over Berg (5,984,988) in light of Eisenberg (4,393,021) and in further view of the rejections of Claims 2 and 11.
- 5) Claims 7 and 16 have been finally rejected under 35U.S.C. 103 (a) as unpatentable over Berg (5,984,988) in light of Culler (6,521,004) and the Quadro Engineering Incorporated Comil® product description.
- 6) Claims 9 and 10 have been rejected under 35U.S.C. 103(a) as unpatentable over Berg (5,984,988) in view of Mathews (3,838,998).
- 7) Claims 9 and 10 have been rejected under 35U.S.C. 103(a) as unpatentable over Berg (5,984,988) in view of Cai (Phys Rev Lett. 2202 Dec:89(23):235501.) Cai indicates that “gamma-alumina is known to transform to theta-alumina and finally to alpha-alumina upon thermal treatment. It is asserted to be obvious to choose gamma-alumina as taught by Cai from the Claim 18 material list to be converted into alpha alumina in the thermal treatment set by Berg.
- 8) Claims 19 and 20 Rejected under 35U.S.C. 103(a) as unpatentable over Berg (5,984,988) in view of Culler (6,521,004).

- 9) Claim 19 and 20 have been rejected under 35U.S.C. 103(a) as unpatentable over Berg (5,984,988).
- 10) Claim 21 has been rejected under 35U.S.C. 103(a) as unpatentable over Berg (5,984,988) in view of in view of Ramanath (5,834,569).

ARGUMENTS AND RESPONSE TO THE OFFICE ACTION

- 1) **Claim 9 has been rejected under 35 USC 112, first paragraph as containing subject matter not originally disclosed.**

The subject matter of this claim that was the basis of this rejection is:

“foaming agents, gas-forming substances, and/or blowing agents.”

Claim 9 has been amended, removing specifically that material regarded as unsupported and leaving the material specifically identified as supported. This amendment therefore raises no new issues nor requires further search or examination as the Examiner has already considered the remaining material and the subject matter.

NOTE WITH REGARD TO THE RESPONSES TO THE REJECTIONS BASED ON ART

Rather than merely repeating the arguments previously set forth, which arguments, although responded to by the Examiner, are still believed effective, Applicants will provide an initial section under certain of the rejections that will provide exclusively new arguments for consideration by the Patent and Trademark Office. A heading identifying the arguments as new will be provided.

- 2) **Claims 2, 3, 6, 8, 11, 12, 15 and 17. have been rejected under 35U.S.C § 102(b) as being anticipated by Berg (5,984,988).**

NEW ARGUMENTS REGARDING THIS REJECTION

Berg states that, **and to enable functionality for his process**, his dispersion must be solidified before removal from the cavities in order for the ejected particles to retain the same shape they had as they resided within the cavities; and that the amount of liquid that is removed in this step is 40% or less to achieve this solidification. It is very clear that the removal of 40% of the liquid from the dispersion produces solidified particles, is

intended to produce **solidified particles**; and must produce solidified particles to function according to the disclosure. Therefore these particles do not have a liquid state and therefore are not subject to internal surface tension forces that would re-form them into spherical shapes. **The Berg particles are not liquid, whatever their liquid content. They are solidified and do not anticipate the claims.**

At Column 7, lines 45ff Berg states:

”A **sufficient amount** of the volatile component **MUST BE** removed from the dispersion to **bring about SOLIDIFICATION** thereof, thereby forming a precursor of an abrasive particle having approximately the **same shape as the shape of the mold cavity.**” Further, at Col 7, L53 it is stated “**Typically, up to 40% of the LIQUID is removed from the dispersion...**” (emphasis added)

As Berg solidifies his material, that material cannot anticipate the limitation in the claims that is recited in Claim 2:

“**ejecting the liquid mixture volumes** from the cell sheet by **subjecting the liquid mixture solution** contained in each cell to an impinging jet of fluid wherein the impact of the impinging jet of fluid **dislocates the liquid mixture volumes** from the cell sheet thereby forming independent mixture solution lump entities;...” (emphasis added)

Berg’s “rounding” is simply meant “to break-off a sharp edge” as in to “round it off”. In the Oxford English Dictionary (OED), 2004 “round”, v. is “to make round, convex, or curved by trimming off edges or angle; to cut off (points, etc.) so as to make round.”; and “to become round, circular, OR spherical; to grow or develop to a full round form.”. Also (OED), 2004 refers to “rounding”, vbl. n. as “a rounded edge or surface; a curvature; a curved part or outline; a tonsure”. None of these definitions refer to “rounded” as being exclusively “spherical” and the process shown by Berg **cannot** form a sphere. Such a result of a spherical particle is impossible from the actual methods taught by Berg and there is no motivation to alter the process of Berg and no direction on how to alter the process of Berg to form spherical particles.

RESPONSE TO THE ARGUMENTS OF THE EXAMINER

Further and more importantly, Berg teaches that “the (mold) cavity may be the inverse of even other solid geometric shapes, such as, for example, pyramidal, frusto-pyramidal, truncated spherical, truncated spheroidal, conical, and frusto-conical” (Column 6, lines 35-47). In accordance with the broadest reasonable interpretation of the term “spherical” in the instant claim language, Bergs formation of truncated spherical particles anticipates applicants formation of “independent spherical entities”.

This is a misinterpretation of the word “SPHERICAL”.

In **Berg**, Col 11, L24, he states “If an abrasive particle is prepared in a mold cavity having a pyramidal, conical, frusto-pyramidal, frusto-conical, truncated spheroidal shape, the thickness is determined as follows...(L35) in the case of a truncated sphere or truncated spheroid, the thickness is the length of a line perpendicular to the center of the base of the truncated sphere or truncated spheroid and running to the curved boundary of the truncated sphere or truncated spheroid”. This shows that the “base” is flat and planar (hence the “perpendicular”) in all cases which is totally different than a full-curvature sphere that has no “base.” A truncated spheroid is not spherical.

When a sphere is truncated it is cut into half (or less) sections to form a hemisphere, or even a sphere-cap that has a very limited thickness relative to its diameter. The ONLY types of dispersion “spheroids” (as defined by Berg) are formed out of a single thickness cavity sheet into which he forms (machines) his cavities into the sheet from only one side of the sheet, or completely-through the sheet thickness . He **can not machine-form a spherical cavity inside a thin sheet**. If he did form a spherical cavity inside the sheet thickness he would neither be able to fill this cavity with dispersion or remove the solidified dispersion sphere as there would be no openings from the sphere cavity to either surface side of the cavity sheet. **BERG does not enable formation of a spherical particle and therefore cannot anticipate or render that term obvious.**

For reference, in the Oxford English Dictionary (OED), 2004 “truncate”, v. is “To shorten or diminish by cutting off a part; to cut short; to maim, mutilate”. Also the OED defines “truncated”, ppl. a as “Of a figure: Having one end cut off by a transverse line or plane; esp. of a cone or pyramid: **Having the vertex cut off by a plane section**; esp. one parallel to the base; thus **truncated cone or pyramid=FRUSTUM** of a cone or pyramid.”.

**THE ATTEMPT TO CITE ZHAI et al. AS A TEACHING OF THE
INHERENTCY OF SPHERICITY IN BERG OR THE ABILITY TO RENDER
BERG'S PARTICLES SPHERICAL**

First, the citation of Zhai et al. is not a teaching of inherency, but rather is a teaching of what is purported to be operational modifications that can be performed to render a sol-based particle more round. That citation is legally inapplicable to a rejection under 35 USC 102(b) and any content of Zhai used to suggest changes in Berg are not acceptable in the rejection. Secondly, because of the fundamentally different nature of the processes of Berg and Zhai and the compositions and objectives of Berg and Zhai, inherency is not established. Thirdly, the only way to combine the teachings of Berg and Zhai is to dramatically change the objectives, parameters and process of Berg, which is incompatible with a rejection under 35 USC 102(b).

Zhai Article.

Zhai's article subject process is a **SPRAY PELLETIZATION** or **GRANULATION** process which is a **completely different process** from the **COLLOIDAL GELATION** processes of both Berg and the present invention. Zhai forms his large-sized composite agglomerates from two different small-sized and spherical shaped dried oxide powders because these same small powders can not be successfully used directly for thermal spraying applications. The small sized dual-oxide powders act like dust in the thermal spray process and can't be applied properly to the intended target surface areas. Further, the very smallest oxide powders have a tendency to separate from the larger different-oxide powders, which could cause the thermal spray to apply a coating of either one oxide material or the other. Here, the desired thermal spray coating is a combination of the two different oxide materials.

Zhai's process starts with two different sized and different-material preformed spherical solid oxide balls, mixes them with water and a dispersant, mills them aggressively, adds a binder and again mills the mixture aggressively. He then uses a high speed rotary-wheel spray drier to form enlarged spheres of the composite mixture. The formed spheres are then dried by a heated air atmosphere which evaporates the liquids from the bodies of the agglomerate spheres. Upon liquid evaporation from the spherical formed pellets (granules) that contain the composite previously-solidified oxide spheres, the different individual oxide spheres that form the spherical pellets bond to each other. Each of the resultant spray-pelletization formed individual enlarged agglomerates

consists essentially of a few of the larger spherical particles of one oxide material that are surrounded with many of the very small spherical particles of the other oxide material. For each spherical pellet, the small oxide spheres are in direct surface contact with the large oxide spheres. The resultant large diameter agglomerate spheres have two different (material and size) oxides that are bonded together sufficiently well that they can be used in a thermal spraying operation to apply a uniform coating of both oxides to a workpiece surface.

In Chapter 25 titled “Granulation” by Malcolm Summers and Michael Aulton in the book “Pharmaceutics, 2nd Edition”, edited by Michael Aulton, ISBN 0443055173, Harcourt-International, Pg 364-378, a full description of the process of forming large sized granules from solidified spheres of two different materials having different sphere sizes is made. Pictorial illustrations of the “ball growth” of these enlarged granules from the smaller constituent spheres are clearly shown in various Figures by Summers and Aulton. For instance, Fig. 25.1 “Granulation to prevent powder segregation”, Pg 365, shows the granulation of two different powders into Monosized granules and why the powders are granulated to prevent separation into segregated powders. Fig. 25.2 “Water distribution between particles of a granule during formation and drying”, Pg 368, shows how liquids are positioned relative to the solid constituent spheres during the processes of forming and drying the granules. Fig. 25.3 “Mechanisms of ball growth during granulation”, Pg 370, shows different mechanisms of forming the monosized granules.

When a colloidal dispersion is gelled, the colloidal organic or inorganic particles join together in strings to form fibrous branches that are interconnected into a single lattice-network entity where many of the fibers contact each other. This formation of interconnected fibrous branches during colloidal gelling is well known to those skilled in the art where the gelled product is referred to as a sol-gel.

In an article “Physics...Physics and Chemistry; Electromagnetism; Quantum Mechanics; Group Theory; The Hodograph, Colloids: the fascinating properties of matter that is all surface”, Pg 1-12, by Dr James B. Calvert of the University of Denver, CO., the formation of Gels from colloidal mixtures is described. On Pg 9, L21 it is stated:

”the system gels, forming a wobbly but definitely solid body.” On Pg 9, L33 he states: **”The colloidal phase in a gelatin is fibular, composed of fibers of colloidal cross-section. When a gel set, these fibers form a tangled mass like a pile of brush, that holds the system together.”**

In Section 3 titled “Sol-gel chemistry and engineering background” Subsection 3.3 “Gelation, aging, drying and firing” in the University of Bordeaux, France Class notes titled “Introduction to Hybrid Organic-Inorganic Materials (12h)” by Etienne Duguet. Pictorial illustrations of the “branched cluster” of colloidal sols that are gelled are shown in Fig. 2, Pg 3-9 “Polymer growth and gel formation in acid-catalyzed systems (polymeric gel)” and in Fig. 4 “Polymer growth and gel formation in base-catalyzed systems (colloidal gel).”

In an April 6, 2004 article “Silica Aerogels: How Silica Aerogels are Made” by M. Ayers from the Ernest Orlando Lawrence Berkeley National Laboratory, CA., a description of an Alcogel is given on L19, “Alocgel (wet gel)” and on L21 “An alcogel consists of two parts, a solid part and a liquid part. The solid part is formed by the three-dimensional network of linked oxide particles. The liquid part (the original solvent of the Sol) fills the free space surrounding the solid part”

In an article titled “Simulations of sol gel materials” by Lev David Gelb Research Group Home Page at Washington University in St. Louis, Mo., modified Sep 25, 2006, pages 1-13, a number of schematic morphologies and micrographs of sol gels are shown on page 3 (Adapted from Brinker and Scherer, Sol Gel Science, chapter 9, figures 3a-3d). These figures clearly show the formation of branches of particles where the braches are joined together to form gelled clusters.

These figures clearly show that the granulation (pelletization) process of **Zhai** which forms large sized spherical balls is **totally different** than the colloidal dispersion and sol-gel fibrous forming drying **process of Berg. THEREFORE, ZHAI CANNOT ESTABLISH ANY BASIS FOR INHERENCY AND ITS COMBINATION WITH BERG AS A TEACHING OF WHAT IS INHERENT IN BERG IS CLEAR LEGAL ERROR.**

Furthermore, as Berg is now clearly established as different from Zhai and that there is no inherency in the ability or actuality of sphere formation, and because Berg requires solidification before particle formation in a mold that cannot provide spheres, the rejection has been shown to be clearly in error and the rejection must be withdrawn.

Berg forms a matrix of interconnected oxide particle fibrous branches **DURING GELLATION** that assume his mold cavity shape during his drying process. There is

NO FIBROUS GELLATION of Zhai's mixture during his drying process as his already-solid oxide spheres are simply joined together to form spherical composite granules. As Berg cannot use a spherical three-dimensionally circular mold in his process, but at most can form a hemisphere, and because the particles are ejected as solids while the claims recite ejection as a liquid, the rejection is factually and legally in error.

The % wt of water that is present in Zhai's mixture that allows his rotary wheel spray formation of spherical agglomerates, due to surface tension forces and the fluidity of the mixture, is unique to his mixture of pre-existing solid oxide spheres and water and a binder liquid. It is pure speculation **and not inherency** that the same % wt of water that exists in another unlike dispersion mixture that is comprised of non-solid and non-dried-oxide materials (such as the dispersion mixture in the present invention) would have the same fluidity and reaction to surface tension forces. It is certainly the case that another dispersion mixture unlike Zhai's dispersion mixture, having the same % wt of water, that has already been solidified within a mold cavity before ejection from the cavity (Berg's dispersion), has no capability to be acted upon by surface tension forces to form spherical shapes from the ejected dispersion entities after they are ejected from the individual cavities. Surface tension forces do not act upon solidified entities because they are not liquids. Surface tension forces only act upon entities that are in a liquid state and that have sufficient fluidity to be reshaped by the surface tension forces. Minute rectangular shaped liquid entities having very high viscosities will not form spherical entity shapes in a short period of process time when only acted upon by surface tension forces.

Zhai's high speed rotary spray drier imposes high shearing action forces on his mixture to provide the **purportedly** spherical shapes. Zhai is very careful to provide a dispersion mixture that readily shear-thins to provide these agglomerate beads. His shear-thinned mixture has an extremely high viscosity in the absence of shearing action on the mixture. This zero-shear high viscosity would tend to prevent the formation of spherical shapes of the mixture by surface tension forces alone if no external shear force is applied to the mixture.

By comparison, in the present invention, there are no external shearing forces that are applied to a lump of dispersion mixture that has been ejected from a screen cell

into a drying environment where the dispersion entity lumps are simply SUSPENDED in the drying (dehydration) environment.

In Berg the dispersion mixture is completely different than the Zhai dispersion. Berg's dispersions are colloidal mixtures of oxide material particles that are suspended in water. When these mixtures are partially dried, the individual oxide material particles join together in strings to form branches that are interconnected and woven together. These oxide particles of Berg are NOT JOINED TOGETHER into solidified spherical oxide shapes as is the case for the Zhai spheres that are the starting basis for the Zhai mixture. **When sufficient water is removed from the Berg mixture entities as they remain in the mold cavities, the mixture gels, and forms a single-entity lattice network, at which time the mixture completely loses its fluidity and conforms to the shape of the mold, which is never a sphere.** The mixture mass is no longer acted upon by surface tension forces in a manner that the entities can be reshaped by the surface tension forces. Berg continues to dry or dehydrate the dispersion entities as they remain in the cavities to assure that the entities retain the mold cavity sharp-edged shapes after the entities are ejected from the cavities. The sharp edges on the ejected entities that were formed by the mold cavities are retained throughout further drying and heat treatment process steps that convert the entities into abrasive particles. These sharp edges on the abrasive particles form the cutting edges of the abrasive particles. If these abrasive particles do not have their sharp edges they are useless for abrading purposes. **At no time is a liquid particle ejected from the mold. Berg fails to teach this fundamental and critical step. Every argument in the rejection attempts to assert and prove that a solidified mass that retains its shape is a liquid. THAT IS ERROR ON ITS FACE.**

A more detailed discussion of Zhai's pelletization process as compared to Berg is given in the following:

Zhai starts with both oven-dried perfectly spherical solid Al_2O_3 and small TiO_2 beads. He mixes them with water and a dispersant, and ball mills this mixture for 4 hours; adds a polyvinyl alcohol (PVA) binder and ball mills the new mixture for an additional 4 hours to form a slurry mixture. He then uses a centrifugal spray drier to form bigger composite beads from this slurry.

A description of Zhai's oxide spheres is given starting at the last word of Pg 1, "Both of the sub-micron Al_2O_3 powders and the nanostructured TiO_2 powders were **PEFECTLY SPHERICAL** in shape. The Al_2O_3 powders have a mean particle size of about 0.6 μm in diameter (a distribution of 0.3-1 μm), and the TiO_2 powders have an average size of about 30 nm in diameter (a distribution of 5-80 nm)."

A description of Zhai's oven drying the individual oxide spheres prior to mixing is given on PG 2, Col 1, L 21, "The starting Al_2O_3 and the TiO_2 powders were **OVEN DRIED AT 120 °C** for 10 h to remove any absorbed water moisture on the surface before being blended in the weight ratio of 97 and 3 % respectively." (emphasis added)

a) Zhai's article was **published almost 2 years after the original filing date of the present application, so its failing to be an actual teaching of inherency also destroys its ability to be used in combination with Berg in a rejection under 35 USC 103(a).**

b) In **Zhai**, a oxide mixture having only 30% water allows surface tension forces to form spherical beads. However, this is not a dehydrated and reacted mass as taught by Berg, but rather is a suspension of pre-existing spherical particles in a water carrier medium. This clearly shows that there **CANNOT BE ANY TEACHING OF INHERENCY IN BERG FROM THE TEACHINGS OF ZHAI. THEY ARE DIFFERENT IN VAST NUMBERS OF WAYS AND THERE CANNOT BE ANY SCIENTIFIC BASIS OF INHERENCY BETWEEN THE REFERENCES.**

c) The Examiner concludes (from Zhai's spheres formed by surface tension acting on 30% liquid slurry) that Berg's slurry mixture having 40% liquid will also be acted upon by surface tension to form spheres. He states that it is therefore obvious to create abrasive spheres from Berg's open-cell cavities. That is complete error. An assumption is made that different amounts of materials, treated differently, under different conditions, with different additional additives, will act the same when it is the intent and result of each disclosure to in fact act differently.

Further Differences Between Zhai and Berg that Obviate Inherency

1) **Zhai starts exclusively with: already-formed and dried perfectly-spherical Al_2O_3 and small TiO_2 beads and ball mill mixes them together for 4 hours with water to form a slurry. Even though they are perfectly round beads to start with, Zhai still has to**

mill them very aggressively for long times to successively get them dispersed in the water.

2) **Berg** starts with a dispersion mixture of: AL_2O_3 precursor particles and water and molds them within a flat surfaced mold to provide specifically molded shapes to the particles.

3) **Zhai** adds a binder, e.g., polyvinyl alcohol (**PVA**), to his ball milled dispersion of solid spherical beads and ball mills this new mixture for additional 4 hours.

A description of Zhai's use of a liquid binder and states that his is a SPRAY PELLETIZATION process given on PG 2, Col 1, L 12, "Polyvinyl alcohol (PVA) and n-butanol were used as binder and antifoam agent, respectively. The **PVA was used for bind strength between particles.....**so that the agglomerated powders were easily prepared and avoided to break in the process of SPRAY PELLETIZATION."

Berg does not use a Binder and his is not a SPRAY PELLETIZATION process.

4) **Zhai** ball mills his mixture for long periods of time. Zhai produces a dispersion mixture, having a special additive (PVA), that has a high solids content that still remains fluid by using Ball Milling for long periods of time (8 hours). This is a very tedious and aggressive form of mixing. It is critical to Zhai that his dispersion remain fluid and particularly that the fluid has a dispersion of separate particles. Berg does not ball mill his dispersion, he simply uses a continuous mixer to make a solution of AL_2O_3 abrasive precursor and water and then reacts and solidifies metal oxides within molds.

5) **Zhai's** dispersion mixture is distinctly unique and very likely to have good fluidity because of this uniqueness and the need to keep the particles dispersed so that they may form a core-shell structure of center spheres and coating spheres. Almost all of the volume of his mixture is composed of the 0.6 avg. micrometer AL_2O_3 beads (97% wt) and little volume is composed of the small 0.03 avg. micrometer TiO_2 beads (3%) that coat the surface of the larger spheres. Zhai's dispersion is somewhat analogous to collecting a bunch of glass marbles together with a few tiny glass beads and mixing the marble and beads with water and a binder. It takes very little wt % of liquid to result here in a dispersion that has good fluidity. This is especially the case when the dense marbles and beads are "perfectly spherical" and; were even pre-dried to assure that the marble and bead smooth surfaces are completely dry before mixing. These adjacent solid spheres have good natural freedom to freely move relative to one and another especially because

the bulk of the mixture is made up of marbles that are so large relative to the small beads (20:1 size ratio). Collectively they can individually roll about each other much as would individual ball bearings in a bucket of ball bearings. But this again is totally different from Berg so that any assertion of inherency is untenable on its face.

Berg starts with a dispersion mixture of: Al_2O_3 precursor particles and water. Only single particles are used, the single particle is not spherical, no coating of particles surfaces with other different particles occurs. Berg solidifies his particles in the absence of significant shear and solidified particles are ejected.

6) **Zhai** uses a high speed centrifugal rotary wheel spray drier that applies a high shear to his liquid dispersion. A description of Zhai's use of a rotary wheel spray drier is on PG 2, Col 1, L 34, "After the slurry preparation was completed, spray drying was used to make agglomerated reconstitution powders. The reconstitution process was carried out by a high-speed centrifugal spray drier." Here, this mixture fluid is highly sheared as it moves along the wall surfaces of the high speed centrifugal drier wheel. [The spray drier in 6,645,624 (Adefris), Col. 6, L24 operates at 25,000 to 45,000 rpm.] This shearing action accelerates the fluid whereby it is ejected into a drying air atmosphere as individual ligament streams that travel at a great velocity. Particles are not ejected as recited in the claims. As these curvilinear high speed dispersion ligament streams contact the heated stationary air, the streams decelerate with high shearing action and break into individual dispersion entities. Both surface tension and air friction shearing forces act upon these moving dispersion entities to form his desired spherical composite-oxide spheres.

The oxide dispersion described by Zhai is subjected to very significant shearing forces in the spray drying pelletization process where the dispersion entities are formed into spherical shapes. In **Zhai's Fig. 3** "Effect of binding content on the rheological behavior of Al_2O_3/TiO_2 ceramic slurry: (a) viscosity curves and (b) flow curves" he shows that his shear-thinned slurry has a viscosity of only 0.02 Pa.s at high shear and in excess of 10.0 Pa.s at zero-shear. The zero-shear condition occurs at rest or when a slurry droplet is suspended in a fluid as is the case in the instant invention. The Zhai viscosity here changes by a factor of 500: 1.

In an article "EXPERIMENTAL STUDY AND NEURAL NETWORK MODELING OF THE LIGAMENT DISINTEGRATION IN ROTARY ATOMIZATION" published in Atomization and Sprays, Vol. 12, pp.107-121, 2002 by

Stephan Sternowsky and Gunther Schulte, University of Bremen, Bremen, Germany the formation of ligament streams of a liquid and the formation of spherical droplets is described. Fig. 2, Pg 111 “(a) Ligament formation and breakup (seen from above). (b) Sketch of ligament path.” shows how a liquid exits a high speed rotary wheel in a ligament stream with high tangential speed and also high radial speed, where the stream breaks up as it is decelerated by air and forms the stream into individual spheres.

Berg simply introduces his dispersion mixture into stationary mold cavities and solidifies the molded dispersion entities while they reside in the cavities. He takes great care to assure that the mold cavity shaped entities are solidified so that they will individually retain the cavity shapes after they are separated from the cavities so that his separated abrasive precursor particles have the required particle sharp edges that are needed to perform abrasive cutting actions. It would be a functional disaster for him if his sharp-edged cavity-separated particles were deformed by surface tension forces that rounded-off his mold-shaped sharp particle edges.

As can be seen, the process of Berg and Zhai are dramatically different, there is absolutely no basis for asserting any degree or type of inherency in the product of Berg from the teachings of Zhai, and Zhai is not available as a reference, if tried to be combined with Berg.

7) **Zhai** optimizes the % quantity of both the Dispersant and the Binder PVA to provide a low viscosity, shear-thinning slurry mixture of the solid oxide spheres for the creation of spherical composite beads using the centrifugal spray drier. Zhai deliberately formulates the dispersant and binder to ASSURE creating a shear thinning fluid mixture which would have a low viscosity at high shear rates.

Zhai REQUIRES the addition of the PVA Binder agent to enable the formation of spherical beads. Just because he achieves adequate shear-thinned fluidity from his unique mixture of solidified oxide spheres and water to allow spherical beads to be produced under very high fluid shear process conditions, this does not mean that Berg's dispersion is sufficiently fluid that it would be acted on by surface tension after ejection from his non-spherical cavities to form spherical bead shapes. Additionally, Berg requires that the composition be solidified within the mold. This is antithetic to remaining a liquid. Berg's material is intended to retain its shape without restraint, which is contradictory to the very definition of a liquid.

Berg does not desire a shear-thinning dispersion mixture that assumes and retains the shapes of his mold cavities. He even prefers that the mixture is the opposite whereby it is gelled, to prevent surface tension from re-forming the assumed cavity shapes of the ejected slurry entities.

8) **Zhai** references the wt % solids in his dispersion. He starts with dried perfectly-spherical Al_2O_3 beads and small TiO_2 beads. He then adds water and binder liquids to form his dispersion. The wt % amount of liquid or solids that he references for his pre-sprayed dispersion is related to the liquid that was added to his solid oxide spheres during the mixing process and not to the remaining liquid after drying as in the case of **Berg**. **Berg** starts with particles of an aluminum oxide monohydrate (boehmite) and simply collects the already-solidified ejected particles for further high temperature heat treatment processes. **Zhai** does not heat-treat his spheres, he simply dries them for final thermal spraying use.

Before addressing the specific limitations in the claims that clearly distinguish the novelty of the present invention as claimed from the disclosure of **Berg**, it is believed to be worthwhile to compare the background technology of **Berg** versus the nature of the invention provided in the present Application. These subsequent arguments are substantially similar to those previously presented in the past correspondence. **It must be noted that a major point of error in the rejection is the repeated assertion that “solidified” materials of Berg that are intended to and must retain their shapes in the absence of a restraining environment are being asserted as a liquid. That assertion is contrary to the most basic definitions used in Physics and Chemistry for the properties of a liquid.**

BERG

Berg manufactures individual sharp-edged abrasive particles directly from precursor aluminum oxide material. To produce the abrasive particles the disclosure teaches filling sheet cavity through-holes with an alpha alumina precursor dispersion mixture solution to manufacture hardened abrasive particles having sharp edges from the alpha alumina. Some of the sheets have flat-surfaced through-hole cavities that provide sharp edges to the dispersion entities that are contained in the level-filled sheet cavities.

The volume of each of the liquid-state dispersion entities is equal to the contained-volume of the corresponding individual cavity holes.

The entity geometric shapes are initially established when the entities are formed by the mold cavities. The ejected shrunken entities have the same shapes as the mold cavities; the same-shape entities are just smaller than before they were shrunk. The cavity holes act as molds to shape each individual entity with entity-flat surfaces that intersect each other at angles that are approximately 90 degrees, or less, to form sharp knife-like edges at the intersections of the flat surfaces of each entity. The abrasive precursor entities are then solidified while they are in residence within the confines of the mold cavities so that most of the individual dispersion entities retain all of their sharp edges after they are ejected from the cavity molds. **The shapes must retain these sharp edges as that is the function and intended purpose of the Berg process.**

During the process of solidification of the dispersion entities by drying, while they reside within the cavity molds, the dispersion experiences significant shrinkage due to the loss of water from the dispersion as a result of the drying process. The Berg dispersion typically loses 40% of the water during the in-cavity drying process. The shrunken entity, however, retains and must retain the general geometric shape of the non-shrunken entity, especially including the sharp entity edges. Because the shrunken dispersion entity is now smaller than the mold due to this shrinkage, gravity alone provides a sufficiently large force on the shrunken entities that they freely fall out of the mold cavities. Berg also describes the use of a “low pressure” to aid in the entity ejection from the mold cavities. It is important to the reference that the ejected dispersion entities retain the sharp entity edges and general entity geometric configurations after entity ejection.

Some further entity shrinkage after mold ejection takes place during the calcining and sintering heat treatment steps. The hardened abrasive particles that are produced by this mold cavity process are used directly as abrasive particles that still have the same shape as their mold-ejected entities. The mold-formed sharp edges are used to cut away workpiece material when these hardened entities are in abrading contact with a workpiece. These hardened abrasive particles are coated as-is on abrasive articles; they are not broken or crushed prior to coating to develop new sharp cutting edges prior to coating on an abrasive article.

There is of course absolutely no teaching in Berg of using “excessive” ejection forces to dislodge particles. Such a teaching would be destructive of the intent of Berg to form particles of specific functional shapes to enable his technology. If significantly large ejection forces are applied to his dispersion entities to dislodge them from the mold cavities with **any effective result** that the sharp edges of the individual dispersion entities become rounded, the resultant non-sharp rounded edges would lose the abrasive cutting capability that is the objective of Berg. It is well established that it cannot be obvious to destroy the benefits and function taught by a reference for no benefit, and it is further unreasonable to assert that it is inherent that excessive forces would be used that destroy the function of the reference, with the sole purpose being to meet the limitation of the pending application. The edge-rounding of the ejected particle of Berg would have to be a single one-time event that occurs at the time that the particle is ejected from the mold cavity, as once the semi-hardened shape had been obtained, no other forces are likely to occur to reshape the molded shape of the ejected particles. No such forces are taught by Berg.

It is to be further noted that any of the Berg indicated “Rounding” of some (only) of the sharp edges of the dispersion precursor entities can occur when a through-hole mold cavity is filled to an overflowing condition is not a teaching of the formation of a **spherical particle as recited in claim 2. Merely rounding the edges of a sharp edged shaped particle, in which sharp edges are an objective of the Berg teaching is not the provision of a spherical particle.**

In this *de minimis* teaching of Berg, an undesirable part of the dispersion extends past the sharp cavity-shape delineation edges onto the flat between-hole surface of the cavity sheet. Even though the main body of dispersion entity that is contained in the mold cavity shrinks away from the cavity walls prior to ejection, the overflow-portion of the dispersion entity extends along the sheet surface in an overhanging fashion to form a thin lip that extends out from the body of the entity. Because the thin lip extends past the cavity opening, gravity does not supply enough force to fracture this overhanging lip to allow the shrunken entity to freely drop out of the mold cavity. Berg’s application of a low pressure only to the near-side (pressure side) of the sheet cavities results in an entity ejection force that is applied externally only to the near-side of the dispersion entity that is retrained from freely passing through a mold cavity through-hole. The application of entity ejection pressures is a single-event occurrence. This externally-applied pressure

force breaks off the thin overhanging dispersion lip from the dispersion entity body thereby rounding- off the entity body but only at the locations of the over hanging lips. **This does not produce anything that anyone skilled in the art would consider to be a spherical particle as recited in claim 2.** The reduced-size body at these lip sites allows the dispersion entity to pass through the cavity opening. All of the non-lip edges of the entities are not rounded during this entity ejection event. The entity is thus ejected from the cavity **as a non-spherical particle.**

Little, if any, further rounding of the particle edges occurs after the particle is ejected from the mold cavity, and **even any theoretical further rounding is not taught or suggested to destroy the sharp-edged desired structure of Berg to form the spherical particles claimed in claim 2.** The particle ejection forces are no longer applied to the individual ejected particles after ejection. After an entity is separated from the mold cavity structure even application of “high pressure” will not cause further rounding of the entity edges. Here, the ejected entity is already in a substantially solid state.. Any post-ejection applied pressures will not preferentially “chip away” any portion of the solid entity to form it into a spherical shape, and because of the substantially solid state of the particles, moderate time frame external pressures would not reshape the particles to spherical shapes. Ejected sharp-edged precursor solidified entities would remain sharp (and not become rounded) as the sharp edge is required by Berg to produce hardened abrasive particles that individually have many sharp cutting edges. It is unreasonable to assume that Berg allows within his disclosure the operation of process parameters that would destroy the objective of his technology.

The rejections assumption of an extreme case where the rounding effect is presumed, where the entity “assumes” the shape of a sphere and this spherical entity is hardened, all of the cutting edges are lost on this hardened entity. That would destroy the functionality and purpose and disclosed benefit of Berg, and is not taught or inherent in Berg. Also, the sizes of these extreme “spherical” shapes would be random in size. The rounded shaped particles would be smaller in size than the original particles because of the edge material removal during the rounding event. Coating these hard smooth-surfaced spherical shaped aluminum oxide aluminum oxide particles on a backing sheet would not produce an abrasive article that could effectively abrade a workpiece surface “as is.”

BACKGROUND OF DUESCHER

A liquid dispersion mixture comprised of oxide material and water is level-filled in sheet cavity through-holes to establish the controlled volumetric size of each dispersion entity. When the liquid-state dispersion entities having non-spherical shapes are ejected from the mold cavities using a fluid jet, the ejected liquid dispersion entities individually assume spherical shapes due to surface tension forces acting on the entities. If the ejected non-spherical entities were already solidified, as is the case with Berg, then surface tension forces would not re-form the solidified entities into spheres because, in part, solidified entities do not have surface tension forces. Spherical entity shapes are formed from the non-spherical liquid entities that are ejected from the cavities. The non-ejected entities can not have spherical shapes because the level-filling action on the dispersion filled cell through-holes produces flat surfaces on each entity that resides in the cell holes. Spherical entity shapes are formed by the surface tension forces independent of the geometric shape that each mold cavity has. For instance, rectangular or circular mold cavity shapes will both produce a liquid spherical dispersion entity when these flat surfaced liquid entities are acted on by surface tension forces.

Surface tension forces are not “applied forces” that are applied to the external surface of an ejected liquid dispersion entity. Rather, they simply exist within the fluid body. They originate as an artifact of the entity having a liquid-state. Also, surface tension forces do not act on a dispersion entity that is located within a cavity in a manner that would eject the entity from the cavity.

These internal surface tension forces are not to be confused with the external applied fluid-jet forces that are directed to a single external surface of the dispersion entity as it resides in the through-hole cavity. As a fluid jet impinges on the near-side (fluid jet side) of the sheet cavities, a resultant fluid dynamic force is applied externally to the near-side of the dispersion entity. This fluid jet force ejects the dispersion entity out of the cavity whereby the entity exits the far-side of the cavity.

Claim 2, as amended recites:

“...h) wherein the ejected independent liquid mixture solution lump entities are shaped into independent spherical entities by force comprising liquid mixture solution surface tension;

- i) the independent spherical entities are introduced into and subjected to a solidification environment wherein the independent spherical entities become solidified to form loose, green, spherical beads; and
- j) firing the loose, green, spherical beads at high temperatures to produce beads.”

It can be seen from these limitations that the claims recite “spherical particles” (which are not disclosed by Berg as shown in the above arguments, and that liquid entities are ejected from the compartments, which is also clearly not shown by Berg. The claims also recite that the ejected liquid is shaped into a sphere by at least surface tension, again a step not taught by berg. Berg has been clearly shown to fail to teach the totality of limitations of claim 2 as presented above. Neither claim 2 nor any claim dependent therefrom can be rejected under 35 USC 102(b) and this rejection must be withdrawn.

Claim 11 cannot be rejected under 35 USC 102(b) over Berg for the same or similar reasons described above with respect to claim 2. Claim 11 recites:

“...e) mixing materials into a liquid solution, the liquid mixture solution comprising abrasive particles, an inorganic vitrifiable oxide[5] or a combination of inorganic vitrifiable oxides, and water or solvents or a combination thereof;

f) filling the cell sheet holes with the liquid mixture solution to form mixture volumes wherein the volume of mixture solution contained in each mixture volume is equal to the cell sheet volume; i) ejecting the liquid mixture volumes from the cell sheet by subjecting the mixture solution contained in each cell to an impinging jet of fluid wherein the impact of the impinging jet of fluid dislocates the liquid mixture volumes from the cell sheet thereby forming independent liquid mixture solution lump entities;

g) wherein the ejected independent liquid mixture solution lump entities are shaped into independent spherical entities by at least mixture solution surface tension forces;”

Because of the presence of these limitations, the claims cannot be rejected as proposed in the Office Action. The rejection must be withdrawn.

Applicants further disagree with respect to the rejection of claim 11 under this provision with respect to the comments made by the rejection with regard to the green state. Applicants also not, for the record, at this time, that green has no required meaning

of color, but refers to the art-recognized green state of inorganic oxides. Green agglomerates are formed when enough water is removed from the dispersion to form agglomerates that do not stick to each other. Sources of this statement are described in the present specification and are listed here:

1. “Water is removed from the dispersed slurry and surface tension draws the slurry into spheroidal composites to form green composite abrasive granules.” (pg 31, L22ff).
2. “The dehydrated green composite generally comprises a metal oxide or metal oxide precursor, volatile solvent, e.g., water, alcohol, or other fugitives and about 40 to 80 weight percent equivalent solids, including both matrix and abrasive, and the solidified composites are dry in the sense that they do not stick to one another and will retain their shape.” (pg 31, L28ff).
3. “Agglomerate beads are solidified into green state spherical shapes when the water component of the water-based slurry agglomerate is drawn out at the agglomerate surface by the dehydrating liquid or by the heated air.” (pg 146, L20ff).

In addition, Berg states that “It is preferred that a sufficient amount of volatile component be removed from the dispersion so that the precursors of the abrasive particles can be easily removed from the cavities of the mold. Typically, up to 40% of the liquid is removed from the dispersion in this step. At this point the precursors of the abrasive particles are sufficiently nonsticky that they will not stick to one another when they are removed from the mold” (C7, L19ff).

The rejection refers to Berg in a way that is somewhat askew of the issue. The Berg description at (C7, L46-58) does not result in the stated interpretation stated as: “Typically, the precursors of the abrasive particles will be dried (outside of the mold”).

Instead, the (C7, L46-58) statement is, as written:

“The precursors of the abrasive particles can be further dried outside of the mold. If the dispersion is dried to the desired level in the mold, this additional drying step is not necessary. However, in some instances it may be economical to employ this additional drying step to minimize the time that the dispersion resides in the mold. During this additional drying step, care must be taken to prevent cracks from forming in the precursors of the abrasive particles. Typically, the precursors of the abrasive particles will be dried for from about 10 to 480 minutes, preferably from 120 to 400 minutes, at a temperature from about 50°C. to about 160°C., preferably from about 120°C. to about 150°C.” (emphasis and underlining added)

The Berg dispersion particles are in a green state when they are dehydrated sufficiently to **solidify** and to shrink enough to drop out of his mold cavities and where they retain their sharp particle edges. As they are in a green state at the time that they are ejected from the cavities, they cannot thereafter be converted to a green state.

2) Claims 5 and 14 have been rejected under 35U.S.C. 103(a) as unpatentable over Berg (5,984,988) in light of Eisenberg (4,393,021) and in further view of the rejections of Claims 2 and 11.

All rejections of claim dependent from claims 2 and 11 in this rejection are inherently defective for the reasons given above with respect to the failure of Berg to teach the limitations in totality of claims 2 and 11. No additional reference in this rejection has been cited as showing reasons for destroying the function and purpose of Berg that differentiates Berg from the claims subject matter of claims 2 and 11. In the absence of such a specific teaching, this rejection must fail at least for this reason.

Additionally, Eisenberg cannot be combined with Berg without destroying the objectives of Berg. It would not be possible to substitute an Eisenberg woven screen for berg's mold belt to manufacture Berg's dispersion entities. The cells formed by the individual interleaved wire strands in the woven screen are interconnected with adjacent cells. The cells "appear" to be separated by the wire strands as viewed from the top flat surface of the screen. However, the actual screen thickness results from the composite thickness of individual wires that are bent around perpendicular wires where the screen thickness is often equal to three times the diameter of the woven wires. Adjacent "cell volumes" are contiguous across the joints formed by the perpendicular woven wires. Level-filling the screen with Berg's dispersion creates adjacent cell dispersion entities that are joined together across these perpendicular wire joints. When Berg dries his screen-cell entities, the entities shrink and some entities would pull themselves apart from each other at the screen joints. However, the entity shrinkage will not be sufficient that the non-joined solidified entities will pass through the screen openings. The entities will remain lodged in the screen mesh as trapped by the portions of the entity bodies that extended across the woven wire joints. Berg can not use a woven screen to process his dispersion entities.

3) **Claims 7 and 16 have been rejected under 35U.S.C. 103 (a) as unpatentable over Berg (5,984,988) in light of Culler (6,521,004) and the Quadro Engineering Incorporated Comil® product description.**

All rejections of claim dependent from claims 2 and 11 in this rejection are inherently defective for the reasons given above with respect to the failure of Berg to teach the limitations in totality of claims 2 and 11. No additional reference in this rejection has been cited as showing reasons for destroying the function and purpose of Berg that differentiates Berg from the claims subject matter of claims 2 and 11. In the absence of such a specific teaching, this rejection must fail at least for this reason.

There is also a further defect in the teaching of Culler that prevents this rejection from establishing obviousness. **Berg** level fills mold cavities with a liquid dispersion and **solidifies** the dispersion by drying **prior to ejecting** the dispersion cavity entities from the cavities. The shapes of the ejected Berg particles are not changed after ejection. Also, the solidified entities are **not spherical** in shape.

Culler extrudes a mixture of abrasive particles into **filaments** that are solidified and then **broken** into abrasive agglomerate **particles**. The solidified entities are not spherical in shape. Neither the Berg nor Culler processes, or a combination of the Berg and Culler processes, produce ejected liquid abrasive particle filled abrasive dispersion entities that can be acted on by surface tension forces to form the entities into spherical shaped entities. There is no other disclosed mechanism that can be used with the Berg or Culler processes that can produce equal sized spherical abrasive agglomerate beads.

It also would not be obvious to modify Berg's belt mold by substituting Culler's cone screen and impeller. Provision must be made to dry Berg's dispersion entities while they reside in the mold cavities for them to assume the sharp edged three dimensional shape of the cavities before they are ejected. Culler extrudes his dispersion filaments that break off at random lengths which are then hardened and fractured into abrasive particles.

Furthermore, it would not be obvious to incorporate (sharp) diamond particles into the erodible matrix material of the Berg invention according to the teachings of Culler. It is not possible or desirable to incorporate individual diamond abrasive particles into solidified hardened aluminum oxide abrasive particles.

4) Claims 9 and 10 have been rejected under 35U.S.C. 103(a) as unpatentable over Berg (5,984,988) (listed as 6,521,004, Culler?) in view of Mathews (3,838,998).

All rejections of claim dependent from claims 2 and 11 in this rejection are inherently defective for the reasons given above with respect to the failure of Berg to teach the limitations in totality of claims 2 and 11. No additional reference in this rejection has been cited as showing reasons for destroying the function and purpose of Berg that differentiates Berg from the claims subject matter of claims 2 and 11. In the absence of such a specific teaching, this rejection must fail at least for this reason.

Additionally, the Mathews reference provides capability that essentially teaches against the possibility of combination with Berg. Berg's process produces solid dispersion entities that are solidified prior to ejection from the mold. The addition of Mathew's bloating agent to Berg's dispersion will not produce solidified hollow beads that are formed while the entities are located in the molds. The particles will still retain the shape of the mold cavities. Berg depends upon his dispersion entities shrinking while they are located in the mold cavities in order that they freely drop out of the cavities. The bloating agent would instead expand the individual entities and prevent their ejection from the Berg mold.

To form equal sized hollow beads, it is necessary to form equal volume entities that are made from a dispersion that contains a "chemical agent" that forms a gas upon heating, ejecting these liquid entities from the mold cavities and then subjecting the now-spherical shaped entities to high temperatures. The high temperatures form the hollow spheres and also vitrify the beads to produce glassy surfaces.

5) Claims 9 and 10 have been rejected under 35U.S.C. 103(a) as unpatentable over Berg (5,984,988) in view of Cai (Phys Rev Lett. 2202 Dec:89(23):235501.) Cai indicates that "gamma-alumina is known to transform to theta-alumina and finally to alpha-alumina upon thermal treatment. It is asserted to be obvious to choose gamma-alumina as taught by Cai from the Claim 18 material list to be converted into alpha alumina in the thermal treatment set by Berg.

All rejections of claim dependent from claims 2 and 11 in this rejection are inherently defective for the reasons given above with respect to the failure of Berg to teach the limitations in totality of claims 2 and 11. No additional reference in this rejection has

been cited as showing reasons for destroying the function and purpose of Berg that differentiates Berg from the claims subject matter of claims 2 and 11. In the absence of such a specific teaching, this rejection must fail at least for this reason.

6) Claims 19 and 20 Rejected under 35U.S.C. 103(a) as unpatentable over Berg (5,984,988) in view of Culler (6,521,004).

All rejections of claim dependent from claims 2 and 11 in this rejection are inherently defective for the reasons given above with respect to the failure of Berg to teach the limitations in totality of claims 2 and 11. No additional reference in this rejection has been cited as showing reasons for destroying the function and purpose of Berg that differentiates Berg from the claims subject matter of claims 2 and 11. In the absence of such a specific teaching, this rejection must fail at least for this reason and the other reasons given above with respect to Culler.

7) Claim 19 and 20 have been rejected under 35U.S.C. 103(a) as unpatentable over Berg (5,984,988).

All rejections of claim dependent from claims 2 and 11 in this rejection are inherently defective for the reasons given above with respect to the failure of Berg to teach the limitations in totality of claims 2 and 11. No additional reference in this rejection has been cited as showing reasons for destroying the function and purpose of Berg that differentiates Berg from the claims subject matter of claims 2 and 11. In the absence of such a specific teaching, this rejection must fail at least for this reason.

8) Claim 21 has been rejected under 35U.S.C. 103(a) as unpatentable over Berg (5,984,988) in view of in view of Ramanath (5,834,569).

All rejections of claim dependent from claims 2 and 11 in this rejection are inherently defective for the reasons given above with respect to the failure of Berg to teach the limitations in totality of claims 2 and 11. No additional reference in this rejection has been cited as showing reasons for destroying the function and purpose of Berg that differentiates Berg from the claims subject matter of claims 2 and 11. In the absence of such a specific teaching, this rejection must fail at least for this reason.

Additionally, it would not be obvious to incorporate Ramanath's color-coding scheme to the abrasive particles of the Berg process to produce spherical abrasive agglomerate beads.

Additional Comments

The reference to the Howard teachings in the rejections is non-instructive assertion that liquid extraction would further render obvious the process of the claims. It would not be obvious to solidify Berg's abrasive precursor entities in Howard's dehydrating liquid. Berg's mold cavities would have to be filled with the liquid dispersion and then the mold would have to be submerged in the liquid to solidify and shrink the dispersion entities while the entities reside in the mold cavities. There are many unknown technology issues related to the processes of solidifying, shrinking and ejecting the solidified entities while submerged in a liquid environment as compared to the simple Berg-described processes that take place in a heated air environment. There are further potential process complications related to a liquid system in general. These include the application of pressure forces to dislodge submerged cavity-trapped entities, the collection of submerged ejected entities, the separation of the liquid from the entities and the facility provision of liquid process equipment that handles explosive liquids or hot oils.

It is speculation that the substitute use of a liquid environment provides any attractive benefits as compared to the Berg hot air environment that would make it obvious to substitute a liquid dehydrating system for Berg's hot air system.

The final fault in this reference is that no matter how liquid is extracted from the materials of Berg while they are in the cavities, they will then retain their **necessary and required sharp-edged state. Liquids, as recited in the claims, do not retain shape unless confined.** The reference and resulting process would still not meet the limitations argued above with respect to the lack of teaching of removal of liquid mass from cavities, subsequent spheroidal shaping, and subsequent green state formation. The Howard reference cannot correct the underlying defects of the Berg reference.

CONCLUSIONS

Applicant has fully responded to the Office Action and elected a single species for examination, **without traverse**. All rejections have been traversed.

All claims are believed to be in condition for allowance.

Authorization is hereby given to charge any additional fees or credit any overpayments that may be deemed necessary to Deposit Account Number 50-1391.

Respectfully submitted,

WAYNE DUESCHER

By His Representatives,

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Date: 5 February 2007

By: 

Mark A. Litman

Reg. No. 26,390

CERTIFICATE UNDER 37 C.F.R. 1.8: The undersigned hereby certifies that this Transmittal Letter and the paper, as described herein, are being deposited in the United States Postal Service, as first class mail, with sufficient postage, in an envelope addressed to: Mail Stop AF, Commissioner for Patents, PO Box 1450, Alexandria, VA 22313-1450 on 5 FEBRUARY 2007.

Mark A. Litman 
Name


Signature



ERNEST ORLANDO LAWRENCE BERKELEY NATIONAL LABORATORY

How Silica Aerogels Are Made

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The discussion below relies upon the following terms:

Hydrolysis:

The reaction of a metal alkoxide ($M-OR$) with water, forming a metal hydroxide ($M-OH$).

Condensation:

A condensation reaction occurs when two metal hydroxides ($M-OH + HO-M$) combine to give a metal oxide species ($M-O-M$). The reaction forms one water molecule.

Sol:

A solution of various reactants that are undergoing hydrolysis and condensation reactions. The molecular weight of the oxide species produced continuously increases. As these species grow, they may begin to link together in a three-dimensional network.

Gel Point:

The point in time at which the network of linked oxide particles spans the container holding the Sol. At the gel point the Sol becomes an Alcolgel.

Alcolgel (wet gel):

At the gel point, the mixture forms a rigid substance called an alcolgel. The alcolgel can be removed from its original container and can stand on its own. An alcolgel consists of two parts, a solid part and a liquid part. The solid part is formed by the three-dimensional network of linked oxide particles. The liquid part (the original solvent of the Sol) fills the free space surrounding the solid part. The liquid and solid parts of an alcolgel occupy the same apparent volume.

Supercritical fluid:

A substance that is above its critical pressure and critical temperature. A supercritical fluid possesses some properties in common with liquids (density, thermal conductivity) and some in common with gases (fills its container, does not have surface tension).

Aerogel:

What remains when the liquid part of an alcolgel is removed without damaging the solid part (most often achieved by supercritical extraction). If made correctly, the aerogel retains the original shape of the alcolgel and at least 50% (typically >85%) of the alcolgel's volume.

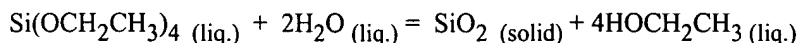
Xerogel:

What remains when the liquid part of an alcolgel is removed by evaporation, or similar methods. Xerogels may retain their original shape, but often crack. The shrinkage during drying is often extreme (~90%) for xerogels.

Sol-Gel Chemistry

The formation of aerogels, in general, involves two major steps, the formation of a wet gel, and the drying of the wet gel to form an aerogel. Originally, wet gels were made by the aqueous condensation of sodium silicate, or a similar material. While this process worked well, the reaction formed salts within the gel that needed to be removed by many repetitive washings (a

long, laborious procedure). With the rapid development of sol-gel chemistry over the last few decades, the vast majority of silica aerogels prepared today utilize silicon alkoxide precursors. The most common of these are tetramethyl orthosilicate (TMOS, $\text{Si}(\text{OCH}_3)_4$), and tetraethyl orthosilicate (TEOS, $\text{Si}(\text{OCH}_2\text{CH}_3)_4$). However, many other alkoxides, containing various organic functional groups, can be used to impart different properties to the gel. Alkoxide-based sol-gel chemistry avoids the formation of undesirable salt by-products, and allows a much greater degree of control over the final product. The balanced chemical equation for the formation of a silica gel from TEOS is:



The above reaction is typically performed in ethanol, with the final density of the aerogel dependent on the concentration of silicon alkoxide monomers in the solution. Note that the stoichiometry of the reaction requires two moles of water per mole of TEOS. In practice, this amount of water leads to incomplete reaction and weak, cloudy aerogels. Most aerogel recipes, therefore, use a higher water ratio than is required by the balanced equation (anywhere from 4-30 equivalents).

Catalysts

The kinetics of the above reaction are impracticably slow at room temperature, often requiring several days to reach completion. For this reason, acid or base catalysts are added to the formulation. The amount and type of catalyst used play key roles in the microstructural, physical and optical properties of the final aerogel product.

Acid catalysts can be any protic acid, such as HCl. Basic catalysis usually uses ammonia, or, more commonly, ammonia and ammonium fluoride. Aerogels prepared with acid catalysts often show more shrinkage during supercritical drying and may be less transparent than base catalyzed aerogels. The microstructural effects of various catalysts are harder to describe accurately, as the substructure of the primary particles of aerogels can be difficult to image with electron microscopy. All show small (2-5 nm diameter) particles that are generally spherical or egg-shaped. With acid catalysis, however, these particles may appear "less solid" (looking something like a ball of string) than those in base-catalyzed gels.

As condensation reactions progress the sol will set into a rigid gel. At this point, the gel is usually removed from its mold. However, the gel must be kept covered by alcohol to prevent evaporation of the liquid contained in the pores of the gel. Evaporation causes severe damage to the gel and will lead to poor quality aerogels.

Single-Step vs. Two-Step Aerogels

Typical acid or base catalyzed TEOS gels are often classified as "single-step" gels, referring to the "one-pot" nature of this reaction. A more recently developed approach uses pre-polymerized TEOS as the silica source. Pre-polymerized TEOS is prepared by heating an ethanol solution of TEOS with a sub-stoichiometric amount of water and an acid catalyst. The solvent is removed by distillation, leaving a viscous fluid containing higher molecular weight silicon alkoxy-oxides. This material is redissolved in ethanol and reacted with additional water under basic conditions until gelation occurs. Gels prepared in this way are known as "two-step" acid-base catalyzed gels. Pre-polymerized TEOS is available commercially in the U.S. from Silbond Corp. (Silbond H-5).

These slightly different processing conditions impart subtle, but important changes to the final aerogel product. Single-step base catalyzed aerogels are typically mechanically stronger, but more brittle, than two-step aerogels. While two-step aerogels have a smaller and narrower pore size distribution and are often optically clearer than single-step aerogels.

Aging and Soaking

When a sol reaches the gel point, it is often assumed that the hydrolysis and condensation reactions of the silicon alkoxide reactant are complete. This is far from the case. The gel point simply represents the time when the polymerizing silica species span the container containing the sol. At this point the silica backbone of the gel contains a significant number of unreacted alkoxide groups. In fact, hydrolysis and condensation can continue for several times the time needed for gelation. Failure to realize, and to accommodate this fact is one of the most common mistakes made in preparing silica aerogels. The solution is

simple--patience. Sufficient time must be given for the strengthening of the silica network. This can be enhanced by controlling the pH and water content of the covering solution. Common aging procedures for base catalyzed gels typically involve soaking the gel in an alcohol/water mixture of equal proportions to the original sol at a pH of 8-9 (ammonia). The gels are best left undisturbed in this solution for up to 48 hours.

This step, and all subsequent processing steps, are diffusion controlled. That is, transport of material into, and out of, the gel is unaffected by convection or mixing (due to the solid silica network). Diffusion, in turn, is affected by the thickness of the gel. In short, the time required for each processing step increases dramatically as the thickness of the gel increases. This limits the practical production of aerogels to 1-2 cm-thick pieces.

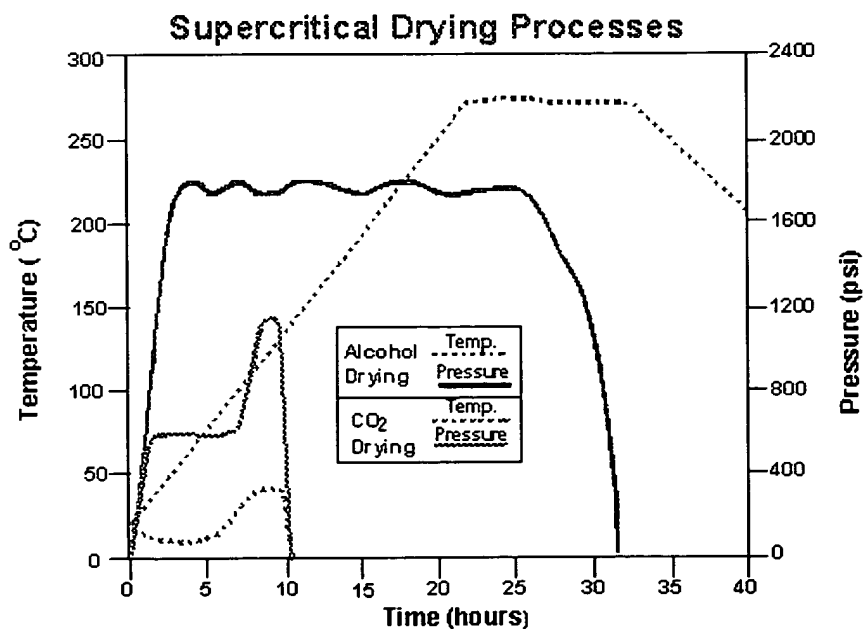
After aging the gel, all water still contained within its pores must be removed prior to drying. This is simply accomplished by soaking the gel in pure alcohol several times until all the water is removed. Again, the length of time required for this process is dependent on the thickness of the gel. Any water left in the gel will not be removed by supercritical drying, and will lead to an opaque, white, and very dense aerogel.

Supercritical Drying

The final, and most important, process in making silica aerogels is supercritical drying. This is where the liquid within the gel is removed, leaving only the linked silica network. The process can be performed by venting the ethanol above its critical point (high temperature-very dangerous) or by prior solvent exchange with CO_2 followed by supercritical venting (lower temperatures-less dangerous). It is imperative that this process only be performed in an autoclave specially designed for this purpose (small autoclaves used by electron microscopists to prepare biological samples are acceptable for CO_2 drying). The process is as follows. The alcogels are placed in the autoclave (which has been filled with ethanol). The system is pressurized to at least 750-850 psi with CO_2 and cooled to 5-10 degrees C. Liquid CO_2 is then flushed through the vessel until all the ethanol has been removed from the vessel and from within the gels. When the gels are ethanol-free the vessel is heated to a temperature above the critical temperature of CO_2 (31 degrees C). As the vessel is heated the pressure of the system rises. CO_2 is carefully released to maintain a pressure slightly above the critical pressure of CO_2 (1050 psi). The system is held at these conditions for a short time, followed by the slow, controlled release of CO_2 to ambient pressure. As with previous steps, the length of time required for this process is dependent on the thickness of the gels. The process may last anywhere from 12 hours to 6 days.

At this point the vessel can be opened and the aerogels admired for their intrinsic beauty.

The graphic below shows the process conditions for both the carbon dioxide substitution/drying process and the alcohol drying process.



Typical Recipes

Single-Step Base Catalyzed Silica Aerogel

This will produce an aerogel with a density of approx. 0.08 g/cm^3 . The gel time should be 60-120 minutes, depending on temperature.

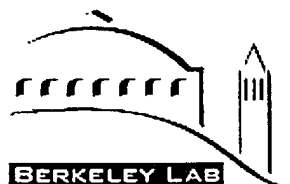
1. Mix two solutions:
 1. Silica solution containing 50 mL of TEOS, 40 mL of ethanol
 2. Catalyst solution containing 35 mL of ethanol, 70 mL of water, 0.275 mL of 30% aqueous ammonia, and 1.21 mL of 0.5 M ammonium fluoride.
2. Slowly add the catalyst solution to the silica solution with stirring.
3. Pour the mixture into an appropriate mold until gelation.
4. Process as described above.

Two-Step Acid-Base Catalyzed Silica Aerogel

This will produce an aerogel with a density of approx. 0.08 g/cm^3 . The gel time should be 30-90 minutes, depending on temperature.

1. Mix two solutions:
 1. Silica solution containing 50 mL of precondensed silica (Silbond H-5, or equivalent), 50mL of ethanol
 2. Catalyst solution containing 35 mL of ethanol, 75 mL of water, and 0.35 mL of 30% aqueous ammonia.
2. Slowly add the catalyst solution to the silica solution with stirring.
3. Pour the mixture into an appropriate mold until gelation.
4. Process as described above.

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

Silica Aerogels

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Note: As of April 02004, this site will no longer be updated. Arlon, after many years of exceptional research and service, has entered a well-deserved state of semi-retirement. Mike, has also moved on to other things. Therefore, you must remain content with its content as it is today. In all honesty, the Light Scattering section of this site, which has been "coming soon" since 1995 will probably never come to fruition. The Lab will keep these pages available for as long as is practically possible, but e-mail inquiries may go unanswered. We hope that you have, and will continue to, find these pages helpful.

M. Ayers April 6, 2004

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1.  [A Brief History of Silica Aerogels](#) By Arlon Hunt and Michael Ayers ([en español](#))
 2.  [At Elevated Pressures](#) (NEW!) A Web biography of the scientist who discovered aerogels, Samuel Kistler. By Michael Ayers
 3.  [How Silica Aerogels are Made](#) A description of the chemical and physical processes used to make silica aerogels. Sample recipes included. ([en español](#))
 4.  [How Do You Work With Aerogels Without Breaking Them?](#) Handle with care. ([en español](#))
 5.  [What if you want them to break?](#) - Silica aerogels will gently absorb the kinetic energy of impacts.
 6.  [The Surface Chemistry of Silica Aerogels](#) A feature of silica aerogels that can have a dramatic effect on their physical behavior.
 7.  [The Pore Structure of Silica Aerogels](#) The pore network of an aerogel constitutes over 95% of its volume.
 8.  [Physical Properties of Silica Aerogels](#) A table of measurements from various sources.

9.  [Optical Properties and Spectrum](#) Silica aerogels are transparent. ([en español](#))
10.  [Thermal Properties](#) The phenomenon most studied for aerogels. ([en español](#))
11.  [Aerogel Nanocomposites](#) Many compositions are possible.
12.  [An Optical Oxygen Sensor](#) A special silica aerogel is at the heart of this device.
13.  [Technology-Transfer Opportunities/Commercial Availability of Aerogels](#)
14.  [The Silica Aerogel Photo Gallery](#) A collection of classic aerogel snapshots. Many are 24-bit color.
15.  [A Partial Bibliography for Silica Aerogels](#) References to technical papers concerning silica aerogels.
16.  [Other Web Sites About Aerogels](#)

Back to the [Microstructured Materials Group HomePage](#) | [Aerogel/Science Questions?](#) | [Webmaster](#)



Solgel Gateway's Site of the month for November 2000!

Gelb Research Group at Washington University in St. Louis

Simulations of Sol Gel Materials

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(The following material is a brief summary of the project description from our NSF grant "Multi simulations of sol-gel materials." - LDG)

Introduction

Silica xerogels are candidate materials for chemical sensors [1,2,3,4,5,6], drug-delivery systems and novel optical [8,9,10,11] and electrochromic[12,13] applications. They are ubiquitous in chromatography [14,15,16] and catalysis [17,18,19], and are widely used in studies of gas separations [20,21] and as a support matrix for nanocluster research [22,23,19].

Aerogels are very high-porosity materials [24,25,26] used in particle detectors and as thermal insulation [27,26], in space probes (for comet-tail dust collection [28]), and in many studies of confined in random media, especially helium and helium mixtures[29,30].

Silica xerogels and aerogels prepared with titanium[31,32], vanadium[33,34,35], or other metal dopants [36], or prepared from other oxides entirely[37,38,17,11,39], are promising materials as catalysts and catalyst supports[17,40,41,42] and in electrochemical applications [38,43] and solar cells [12,44].

Thin films of xerogels can be prepared by a variety of processes, including spin-coating and dip-coating [45]. Thin films are used in sensors, electronics, optics, lubrication, and other areas.

Templated materials arrived in 1992 with the first preparation of "MCM-41" [46], demonstrating that highly regular pore structures could be achieved on scales much larger than those present in nature. Recent developments in templating [47,48,49,50,51,52,53,54] and other micro-patterning technologies[55] suggest the *rational design* of porous media for different applications [56,54]. A variety of microstructures have now been prepared, including arrays of simple geometries, bicontinuous networks, and hierarchical structures [54,57].

More information on sol-gel stuff in general can be found at:

- The [Sol-Gel Gateway](#)
- A [Sol Gel Technology](#) site.

Simulations of gel processing

Simulation models, unlike experimental systems, can be quickly and easily characterized by many methods. In a computational study, the systematic optimization of synthesis conditions as temperature and pH to achieve a desired structure is much less time-consuming than in the real world. Simulations also clearly reveal *why* and *how* particular structures appear. Thus, the development cycle would be greatly accelerated by incorporating the predictive capacity of realistic computer modeling.

We are taking a multi-scale approach in this work, using conventional molecular simulation at up to tens of nanometers and a coarse-grained particulate model at mesoscopic scales up to hundred nanometers.

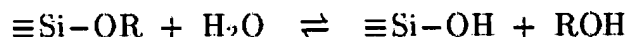
The preparation and properties of xerogels[58,59] and aerogels [27,26] have been comprehensively reviewed. These materials are prepared through sol-gel processing, in which precursor solutions undergo *gelation*, *aging* and *drying*. Xerogels are prepared by drying at subcritical solvent conditions. Liquid-vapor interfaces develop in the drying gel, and forces due to surface tension cause structural changes.

collapse of the gel structure as liquid is removed. Aerogels are dried under *supercritical* (or other [60]) conditions, leading to dry gels with porosity as high as 99.9%. *Consolidation*, or heating at high temperatures, is used to generate densified, non-porous materials for optics and other applications.

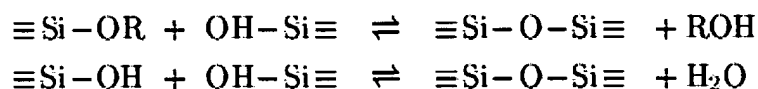
Simulating the preparation of xerogels and aerogels involves separate treatment of gelation, aging, drying, and for non-porous materials, consolidation.

Gelation

In the gelation step, alkoxide gel precursors in aqueous solution are hydrolyzed,



and polymerize through alcohol or water producing condensations:



The gel morphology is influenced by temperature, the concentrations of each species (attention focuses on r , the water/alkoxide molar ratio, typically between 1 and 50), and especially acidity:

- Acid catalysis generally produces weakly-crosslinked gels which easily compact under drying conditions, yielding low-porosity microporous (smaller than 2 nm) xerogel structures (Figure 3a).
- Conditions of neutral to basic pH result in relatively mesoporous xerogels after drying, as rigid clusters a few nanometers across pack to form mesopores. The clusters themselves may be microporous.
- Under some conditions, base-catalyzed and two-step acid-base catalyzed gels (initial polymerization under acidic conditions and further gelation under basic conditions [61,59]) exhibit *hierarchical* structure and complex network topology (Figure 3c).

The initial stages of gelation, when the average cluster size is very small, are best modeled with a purely atomistic approach. Considerable effort has already gone into developing potential models for this, with convincing results [62,63,64,65,66,67,68].

Hierarchically structured gels and low-density gels cannot be directly treated with molecular models; a meso-scale approach must be used in this case. Relatively dense gels can be modeled with *either* atomistic simulations or coarse-grained simulations.

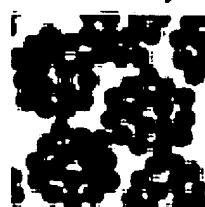
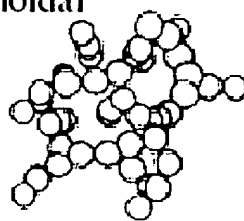
(a) Acid catalysis

*Wet gel (schematic)**xerogel (schematic)**TEM (bar=25nm)*

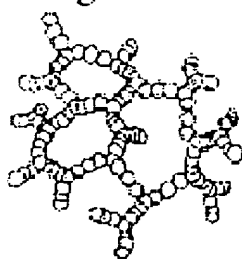
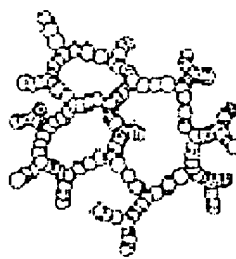
(b) Base catalysis

*Wet gel (schematic)**xerogel (schematic)**TEM (bar=100nm)*

(c) Base-catalyzed colloidal

*hierarchical**random packing**TEM (bar=100nm)*

(d) Aerogel

*Wet gel (schematic)**dried gel (schematic)**TEM (bar=50nm)*

Schematic wet and dry gel morphologies and representative transmission electron micrographs. (Adapted from Brinker and Scherer, *Sol Gel Science*, chapter 9, figures 3a-3d. [58].)

Aging

Gel aging is an extension of the gelation step in which the gel network is reinforced through further polymerization, possibly at different temperature and solvent conditions. *Syneresis*, the expulsion of solvent due to gel matrix shrinkage, can occur during gel aging.

Simulating aging requires the use of an approach which can access long time scales. The "activation-relaxation technique" (ART) [69,70,71] is being implemented for this purpose. In this method the system is repeatedly moved onto saddle-points in the potential energy hypersurface (e.g., "activation") and then relaxed, efficiently sampling many potential minima. These methods have been successfully applied to amorphous silica [70,71] and can be implemented as an extension of a molecular dynamics code. The relaxation step can be accomplished either by numerical optimization or with molecular dynamics.

Drying

The gel drying process consists of removal of water from the gel system, with simultaneous collapse of the gel structure, under conditions of constant temperature, pressure, and humidity.

In the coarse-grained model (below) the equation of state is trivially calculable, and drying is easily modeled by choosing the solvent chemical potential to favor the vapor phase and allowing the particle positions and cell volume to slowly relax under the influence of solvent capillary forces.

At the molecular scale, we can model this process using an extension of the "Gibbs Ensemble Monte Carlo" technique for binary mixtures [72,73,74], where the mixture consists of water and atmosphere. The atmosphere will be modeled as a single-component gas. In this technique, two simulation cells are coupled by mass-exchange moves, in which molecules in one cell are transferred into the other cell. The volumes of the cells fluctuate independently, allowing specification of the pressure. To model constant *humidity*, the water content in the "atmosphere" cell will be controlled by periodic removal of water molecules from the simulation. This is analogous to using dehumidification in an experimental setup, and has the added benefit of requiring only a relatively small "atmosphere" cell.

Consolidation

Xerogels are higher in free energy than conventional amorphous silica (glass) and crystalline silica, as they have a substantial internal surface area and associated surface tension. During heating to temperatures above at least 700 C, the dry gel shrinks substantially and becomes similar to a melt-prepared glass. Many such sintering experiments are done at constant heating rate, which hastens the densification [59,58]. Simulations of consolidation will use molecular models. Both isothermal conditions and constant heating rates can be accessed with standard molecular dynamics simulations and ART as above.

Aerogels

Aerogels can be simulated using the same basic techniques as xerogels, except that the conditions during drying must be chosen above the critical point of the water model. Aerogel systems do not collapse (much) under drying conditions, and supercritical gel drying will be easier to simulate than the subcritical process. High-porosity aerogels are only accessible via the meso-scale model.

Thin films

Experimental studies involving sol-gel *nanocoating* have been reviewed recently by Caruso and Antonietti[54]. The deposition of a gel of several nanometers' thickness upon a surface or nanoparticle allows one to generate novel nanostructured silica materials (via templating, below), or to modify the surface properties of the system. Simulating such processes requires the introduction of the surface or nanoparticle into the simulation cell and suitable intermolecular potentials. For deposition on planar surfaces, as in spin-coating, the concentration of the sol increases as the solvent

evaporates, which can be accounted for using the drying methodology discussed above.

Templated materials

When a gel is formed around a template which is then removed, the process is known as *casting*, and is the most commonly used templating strategy. One may apply casting *twice*, generating a final material with the same structure as the original template; this is reminiscent of the "lost-wax" method of bronze casting[75]. For gelation around a template, suitable models for the template must be introduced.

Our exploratory simulations in this area will focus on two systems with stiff and soft templates, respectively: rigid nanotubes [76], which are easily modeled for these purposes, and the quaternary ammonium surfactants used in preparation of MCM-41 [46], parameterized using the AMBER force field [77].

Meso-scale particulate model and simulations

We are investigating a coarse-grained model for sol-gel materials which replaces each cluster with a single "gel particle", while accounting for size variation of clusters, aggregation through condensation reactions, and solvent effects. The particle-particle interaction will be relatively short-ranged and of a shifted-center Lennard-Jones type, this approximates particle-particle interactions by the van der Waals interactions between atoms *on their surfaces*. Particles may also form bonds upon contact, which are described with Morse-type potentials. Particle sizes of 1-3 nm are appropriate.

The development of a solvent model suitable for drying simulations is not trivial, and will be a major methodological contribution of the proposed work. The solvent in the coarse-grained approach must (a) possess a liquid-vapor phase diagram and reasonable interfacial properties, (b) be computationally inexpensive to solve, and (c) be sufficiently general that solvent properties and solvent-gel interactions can be fit to molecular simulation results. **These requirements can be met with a lattice-gas model solved in the mean field approximation**[78]. The fluid-fluid and fluid-gel interactions will be chosen to mimic atomistic potentials, truncated at a few grid spacings, and parameterized as necessary. Solvent-particle interactions are pairwise-additive, and within the mean-field approximation are simply given by a summation over forces exerted from lattice points within range of a given particle, weighted by the mean-field solution of the densities at those points. In drying simulations, constant pressure can be modeled with volume-change moves in which the simulation cell expands or contracts by one or more lattice spacings.

In strongly inhomogeneous systems, large parts of the simulation cell will be filled with bulk-like water or water vapor. These lattice points can be simply fixed at the appropriate equilibrium densities. This will substantially speed up solution of the model. Specifically, only lattice points within some threshold distance of a gel particle will be considered "active". As long as the pressure is either above condensation or substantially below it, this distance can be as small as several nanometers. The use of more sophisticated multi-scale "multigrid" techniques [79] to improve the performance of the model will be investigated and applied if possible.

Integration of molecular and meso-scale models

Integration of these two approaches requires two types of "translation". The first is the use of the small-scale model to parameterize the large-scale one. [The molecular model parameters could be determined, in principle, *ab initio*, which would introduce a third, subatomic, scale!] The second type of translation moves in the other direction - once the meso-scale model has been used to generate a structure, how can an

atomic-scale description of (part of) that structure be regenerated? This fine-graining is necessary for simulations of molecular-scale processes occurring within a mesoscopic system.

Dense xerogels, which can be treated with both types of simulation, will be used to parameterize the meso-scale model. The initial stages of gelation in the molecular model can be analyzed to create an ensemble of gel particles by tabulation of the size distribution and dispersion of bonding sites. Simulations of the meso-scale model can then be initiated, and its parameters adjusted to obtain agreement of the global structural properties described above.

To reverse the process, one must replace a collection of gel particles with atomistically modeled silica. This is a non-trivial task, since it requires *adding* atomic-scale information to the system, rather than removing it. Two strategies will be employed. In the first, the particle configuration will be used as a template for "carving" the atomistic model from a block of amorphous silica, modeled separately. Such templating schemes have been effectively used for MCM-41 type materials [80], with molecular simulation used to equilibrate the unrelaxed surfaces. In the second approach, an ensemble of molecular clusters can be extracted from molecular simulations and used to replace gel particles in the coarse-grained model, matched according to size and arrangement of bonding sites. This would result in a molecular model where only inter-cluster interactions are unrelaxed; molecular dynamics can then be used to achieve mechanical stability.

Thus, in modeling the synthesis of a hierarchically structured or low-density material, we begin with molecular simulations of the gelation step. When the length-scale of aggregation in this simulation exceeds a threshold fraction of the cell size, the simulation would switch over to a coarse-grained model *with equivalent statistical properties*, in a much larger cell. This would be used for the remainder of gelation, aging, and drying. For characterizations by gas adsorption or surface structural analysis, a molecular model could be regenerated from the final coarse-grained configuration. For small-angle scattering or network analysis, either regenerated molecular models or meso-scale models could be used.

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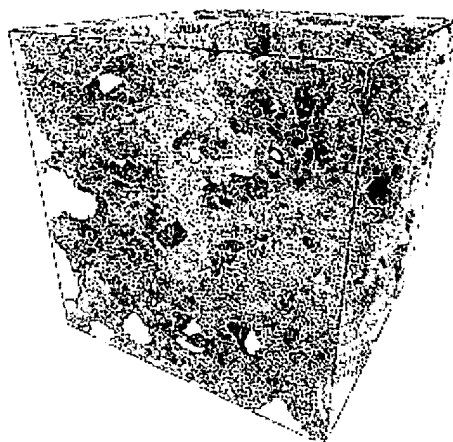
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